

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-257351  
 (43)Date of publication of application : 08.10.1996

(51)Int.Cl. B01D 53/56  
 B01D 53/34  
 B01D 53/81

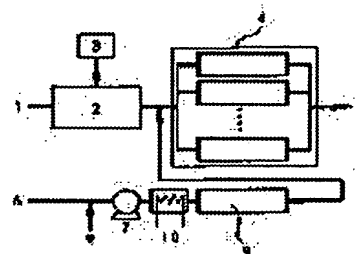
(21)Application number : 07-067336  
 (22)Date of filing : 27.03.1995

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**(54) SYSTEM AND PROCESS FOR TREATING LOW CONCENTRATION NO<sub>x</sub>-CONTAINING GAS****(57)Abstract:**

**PURPOSE:** To purify NO<sub>x</sub> on an adsorbent and make the same harmless without adding a purifying catalyst by providing a dust removing device for removing a dust component in exhaust gas and an adsorption device for adsorbing and removing NO<sub>x</sub>, feeding a reducing agent at the time of regenerating the adsorption device and reduce, and decompose desorbed NO<sub>x</sub> thus adsorbed in the device.

**CONSTITUTION:** Exhaust gas 1 mixed with ozone synthesized by an ozonizer 3 in an oxidization process 2 to oxidize a part or the whole of NO and convert the same into NO<sub>2</sub>. Exhaust gas is introduced into an adsorption layer 4 to adsorb and remove NO<sub>x</sub> and discharged 5 into atmosphere. In the case when a unit with lowered adsorption capability is regenerated on the adsorption layer 4 composed of a plurality of units, nitrogen 6 is introduced into the adsorbent regenerating process by a fan 7, and flowed into an adsorption unit 8 extracted from the adsorption layer 4. Then hydrocarbon 9 is introduced when the oxygen density in the unit 8 is lowered sufficiently, and heated by a heater 10 to reduce and decompose NO<sub>x</sub> by using hydrocarbon.

**LEGAL STATUS**

[Date of request for examination]  
 [Date of sending the examiner's decision of rejection]  
 [Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]  
 [Date of final disposal for application]  
 [Patent number]  
 [Date of registration]  
 [Number of appeal against examiner's decision of rejection]  
 [Date of requesting appeal against examiner's decision of rejection]  
 [Date of extinction of right]

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## CLAIMS

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### [Claim(s)]

[Claim 1] The processing system of the low concentration NOx content gas characterized by having the dust collector from which the dust component in exhaust gas is removed, the adsorber which carries out adsorption treatment of the NOx, and the control unit which supplies a reducing agent at the time of playback of this adsorber, and understands to nitrogen NOx by which uptake was carried out a returned part within this adsorber at the time of desorption.

[Claim 2] They are a part or all of NO in exhaust gas with NO oxidation system after a dust collector removes the dust component in exhaust gas NO2 Processing system of the low concentration NOx content gas which oxidizes, carries out adsorption treatment of the NOx with an adsorber, supplies a reducing agent at the time of playback of this adsorber, and is characterized by understanding to nitrogen NOx by which uptake was carried out a returned part within this adsorber at the time of desorption.

[Claim 3] They are a part or all of NO in exhaust gas with NO oxidation system after a dust collector removes the dust component in exhaust gas NO2 It oxidizes. Desorption of the NOx by which carried out adsorption treatment of the NOx with the adsorber, and supplied the gas containing a reducing agent at the time of playback of this adsorber, and uptake was carried out is carried out. The processing system of the low concentration NOx content gas characterized by introducing into NOx reductor after carrying out reduction decomposition of the part within this adsorber at nitrogen, and carrying out reduction clarification of the remainder of said desorption NOx with this NOx reductor.

[Claim 4] Low-concentration NOx content gas is contacted to an adsorbent, the equipment which reduces the oxygen density in the gas which circulates this adsorbent at the time of playback of an adsorbent in the system which carries out adsorption treatment of the NOx is formed, a content oxygen density is reduced with this equipment, the gas containing brown-coal-ized hydrogen or alcohols circulates, and it is NOx on an adsorbent. N2 The processing system of the low-concentration NOx content gas characterized by what is understood a returned part.

[Claim 5] In the processing system of low concentration NOx content gas according to claim 4, the inert gas which contains a hydrocarbon or alcohols at the time of playback of an adsorbent is circulated, and it is NOx on an adsorbent N2 Processing system of the low concentration NOx content gas characterized by what is understood a returned part.

[Claim 6] Low concentration NOx content gas is contacted to an adsorbent, the gas containing a reducing agent is circulated in the approach of carrying out adsorption treatment of the NOx at the time of playback of an adsorbent, and it is NOx on an adsorbent N2 Art of the low concentration NOx content gas characterized by what is understood a returned part.

[Claim 7] The art of the low concentration NOx content gas characterized by a reducing agent being a hydrocarbon or alcohols in the art of low concentration NOx content gas according to claim 6.

[Claim 8] The art of the low concentration NOx content gas characterized by a reducing agent being the decomposition product of a urea or a urea in the art of low concentration NOx content gas according to claim 6.

[Claim 9] The art of the low concentration NOx content gas characterized by reproducing in the

art of low concentration NOx content gas according to claim 6 by adjusting the temperature of the adsorbent packed bed at the time of adsorbent playback to 100 degrees C - 500 degrees C.  
[Claim 10] The art of the low concentration NOx content gas characterized by an adsorbent having a catalysis to the reaction of NOx and a reducing agent in the art of low concentration NOx content gas according to claim 6.

[Claim 11] Low concentration NOx content gas is contacted to an adsorbent, the gas containing a reducing agent is circulated in the approach of carrying out adsorption treatment of the NOx at the time of playback of an adsorbent, and they are a part of NOx on an adsorbent N2 Art of the low concentration NOx content gas characterized by having carried out reduction decomposition and preparing a NOx reduction decomposition process in the back wash of an adsorbent.

[Claim 12] The art of the low concentration NOx content gas characterized by what is understood a returned part to N2 at the NOx reduction decomposition process prepared in back wash after contacting low concentration NOx content gas to an adsorbent, circulating the gas which contains the compound which promotes desorption of NOx in the approach of carrying out adsorption treatment of the NOx at the time of playback of an adsorbent and desorbing NOx from an adsorbent.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

**[0001]**

**[Industrial Application]** This invention relates to the processing system of the low concentration NOx content gas which removes efficiently low-concentration NOx especially contained in the tunnel for automobiles, a subway way, ventilation gas, etc. from an inside-of-a-house motor pool, and its art about the clearance approach of the nitrogen oxides (NOx) contained in atmospheric air.

**[0002]**

**[Description of the Prior Art]** Generally as the defanging clearance approach of NOx in exhaust gas, ammonia is added to NOx content exhaust gas in a thermal power station, and it is N<sub>2</sub> [harmless on a catalyst]. The selective catalytic reduction process to decompose is mainly applied, and the approach of on the other hand understanding NOx a returned part on a three way component catalyst in a gasoline engine vehicle is applied.

**[0003]** Therefore, ammonia is added in the high-concentration NOx content gas heated as an art of thin NOx in atmospheric air after condensing NOx with an adsorbent beforehand, and it is harmless N<sub>2</sub> with a selective catalytic reduction process. The approach (JP,5-78369,B) of decomposing and emitting etc. is proposed.

**[0004]** on the other hand -- the gestalt of NOx -- NO<sub>2</sub> it is -- if, since the clearance by the adsorbent of NOx or the absorption clearance by alkali is comparatively easy also under moisture coexistence It is NO in low-concentration NOx content gas by addition of corona discharge or ozone NO<sub>2</sub> It oxidizes. This NO<sub>2</sub> It is [ the approach of carrying out absorption clearance by the alkaline lean solution, and ] NO by ozonate NO<sub>2</sub> It oxidizes and is this NO<sub>2</sub>. The approach of carrying out adsorption treatment etc. is proposed (JP,6-99030,A).

**[0005]**

**[Problem(s) to be Solved by the Invention]** This invention is the approach of removing efficiently low-concentration NOx which solves the fault of the above-mentioned conventional technique and is contained in the tunnel for automobiles, a subway way, ventilation gas, etc. from an inside-of-a-house motor pool.

**[0006]** Each conventional technique is the approach which was economical and was excellent, when reaction temperature is usually 200 degrees C or more and processes hot exhaust gas, but adaptation is difficult when [ of ordinary temperature like tunnel ventilation gas ] processing the gas of a large quantity moreover. therefore, as an art of thin NOx in atmospheric air Ammonia is added in the high-concentration NOx content gas heated after condensing NOx with an adsorbent beforehand, and it is harmless N<sub>2</sub> with a selective catalytic reduction process. By the approach of decomposing and emitting 90% or more of NOx generally discharged in these atmospheric air is NO lacking in adsorbent, and since the adsorption engine performance of NO will get extremely bad if moisture moreover contains in raw gas, it is usually necessary to dehumidify it beforehand from raw gas. Therefore, a desiccant is needed besides a NOx adsorbent and there is a trouble of causing processing cost lifting.

**[0007]** furthermore, the gestalt of NOx -- NO<sub>2</sub> it is -- if, since the clearance by the adsorbent of NOx or the absorption clearance by alkali is comparatively easy also under moisture

coexistence It is [ the approach of oxidizing NO in low-concentration NOx content gas to NO2 by addition of corona discharge or ozone, and carrying out absorption clearance of this NO2 by the alkaline lean solution, and ] NO by ozonate NO2 It oxidizes and is this NO2. Although there is the approach of carrying out adsorption treatment etc. By these approaches, there is a trouble of consuming a lot of power as energy for oxidizing NO to NO2. Anyway, playback of an adsorbent is needed, when the adsorption capacity force of NOx by the adsorbent is saturated with the removal method of the low concentration NOx by the adsorbent and it stops showing predetermined NOx clearance effectiveness. Usually, this playback is performed by heating resurgent gas with a sink to an adsorbent. Therefore, the great energy for heating is needed for playback of an adsorbent, and it is not economical. High-concentration NOx will contain in the resurgent gas which let the adsorbent pass, temperature up is further carried out to predetermined temperature if needed, a reducing agent is added, and it is N2 [ harmless on a denitrification catalyst ]. In decomposing and emitting \*\*\*\*, it is NO2. A case will be absorbed with an alkali solution. for this reason -- new -- a denitrification catalyst -- a column may be required Usually, ammonia and hydrocarbons are proposed by the reducing agent of this denitrification reaction.

[0008]

[Means for Solving the Problem] The following means can attain the above-mentioned trouble. In the processing system from which low-concentration NOx by this invention is removed efficiently, and its art, it is characterized by carrying out by circulating the gas which contains a reducing agent for playback of an adsorbent. Usually, NOx removed by the adsorbent is desorbed as concentration gas by heating playback of an adsorbent, and is N2 at a reduction decomposition process. It understands a returned part. After making the approach, alkali compound, and solution which are disassembled into a reduction decomposition process on a catalyst after adding a reducing agent in concentration NOx content gas absorb, the approach of carrying out reduction processing etc. is proposed. These reduction decomposition processes are applying the approach of this invention, and omitting or simplifying is possible.

[0009] Moreover, the processing system of the exhaust gas containing low-concentration NOx by this invention carries out adsorption treatment of the NOx with an adsorber, and is characterized by understanding Adsorption NOx a returned part within this adsorber to desorption and coincidence at nitrogen at the time of playback of this adsorber. In order to raise the engine performance of an adsorber further, NO oxidation system is installed in the upstream of an adsorber, and it is NO2 in all the all [ a part or ] in exhaust gas. You may oxidize. Moreover, when many dust components are contained in exhaust gas, a dust collector may be prepared in the upstream of an adsorber. In order to raise the NOx clearance engine performance of this system further, a NOx reduction cracking unit may be formed in the lower stream of a river of an adsorber.

[0010] The reducing-agent kind to be used can divide roughly the low-concentration NOx art of this invention into two kinds. One approach is an approach of using the decomposition product of a urea or a urea for a reducing agent, and another approach is an approach of using a hydrocarbon or alcohols.

[0011] When the compound which acts as a reducing agent of NOx into resurgent gas contained according to a detailed examination of this invention person etc., it turned out that playback of an adsorbent is performed promptly. And although high-concentration NOx contains in the usual playback in the gas emitted from an adsorbent at the time of playback, there is the description that reduction clearance of a great portion of NOx is carried out with the reducing agent which is also a desorption accelerator at the time of playback, by the approach of this invention.

[0012] As an adsorbent used for this invention, it is the description to have a reaction acceleration operation with the decomposition product of a urea and a urea, a hydrocarbon or alcohols, and NOx at the time of desorption in addition to NOx adsorption capacity. For example, what added various kinds of matter which has a reaction acceleration operation with a reducing agent and NOx in various kinds of matter with NOx adsorption capacity, such as an alumina, a silica, a titania, a silica alumina, a zeolite, and activated carbon, is used. As these typical things, when using the decomposition product of a urea or a urea for a reducing agent, base metal, such

as noble metals, such as Pt, Rh, and Ru, and V, Mo, W, Cr, Mn, Fe, Co, nickel, Ce, is raised. Moreover, when using a hydrocarbon or alcohols for a reducing agent, base metal, such as noble metals, such as Pt, Rh, Pd, Ru, Au, and Ag, and Co, nickel, Fe, Cu, Mn, Ga, is raised.

[0013] Moreover, in order to raise the adsorption capacity of NO<sub>x</sub>, a desirable approach also adds various kinds of alkali, an alkaline earth, and rare earth. For example, they are Li, Na, K, Mg, calcium, Sr, Ba, La, Ce, etc.

[0014] Furthermore, NO<sub>2</sub> which will be easier to adsorb NO if a catalyst component with NO oxidation engine performance is made to contain Since it changes, and it can adsorb and the adsorption capacity force improves, it is desirable. Usually, noble metals, Co, Mn, etc. are desirable. Moreover, since a perovskite compound also has the adsorption capacity of NO<sub>x</sub> and activity is further shown in the reaction of a hydrocarbon or alcohols, and NO<sub>x</sub> in many cases, he is the candidate of a desirable adsorbent.

[0015] It sets to this approach and is at least a part by addition of corona discharge or ozone about NO in low concentration NO<sub>x</sub> content gas NO<sub>2</sub> After oxidizing, since the adsorption treatment effectiveness of NO<sub>x</sub> increases, the method of contacting this generated NO<sub>x</sub> (NO+NO<sub>2</sub>) content gas to an adsorbent is also an effective approach. Adsorbed NO<sub>x</sub> is not only NO but NO<sub>2</sub>. It does not interfere at all with a gestalt.

[0016] When reproducing an adsorbent by the gas containing a reducing agent, in order to advance efficiently the reaction of desorption of NO<sub>x</sub>, and NO<sub>x</sub>, a hydrocarbon or alcohols, it is desirable that temperature up of the adsorbent is carried out to the temperature of 200–500 degrees C by circulating the gas for playback heated beforehand. Of course, a direct adsorbent may be heated with other means, for example, an electric heater etc. Moreover, it is also a desirable approach to carry out the cyclic use of waste water of the gas for playback within the closed system containing an adsorbent, and to fully carry out reduction clarification of the NO<sub>x</sub> which stuck to the adsorbent. In this case, it is also good to add a reducing agent suitably.

[0017] With a solid-state, into the gas for playback, the urea used as a reducing agent of this invention may carry out fuel-spray mixing, and may be supplied with the gestalt of a water solution. Moreover, the cracking unit of a urea is formed beforehand and the gas which hydrolyzed and generated the urea may be supplied suitably. Amines, such as ammonia and isocyanic acid, can be used as a reducing agent of NO<sub>x</sub> among the decomposition products of a urea. The equipment which supplies a urea under steam existence for example, in a heating system, and the equipment which supplies a urea under steam existence on the heated catalyst for urea decomposition can be used for said cracking unit.

[0018] As a hydrocarbon used for the reducing agent of this invention, simple substances, such as methane, ethane, a propane, butane, ethylene, and a propylene, or mixture like LPG is sufficient. Higher hydrocarbon with of course more many carbon numbers is sufficient, and, of course, mixture, such as a gasoline and kerosene, is sufficient. Moreover, as alcohols, methyl alcohol, ethyl alcohol, propyl alcohol, etc. can be used, and it is not limited to especially the class.

[0019] In the case of a gas, these hydrocarbons or alcohol should just supply into resurgent gas as it is. Moreover, in the case of a liquid or a solid-state, it can supply, after spraying as it is into resurgent gas or melting to a suitable solvent according to the description.

[0020] In the low concentration NO<sub>x</sub> clearance approach of this invention, in case it carries out by circulating the gas which contains a hydrocarbon or alcohols for playback of an adsorbent, regeneration efficiency may improve further by making the oxygen density in gas low. For example, adsorption treatment of the NO<sub>x</sub> is carried out with the adsorbent containing noble metals, such as Pt, Rh, Pd, and Ru, a NO<sub>x</sub> reduction reaction is checked by the oxygen which stuck to the noble-metals front face when circulating the nitrogen gas which contains a hydrocarbon at the time of playback, and reaction effectiveness may fall. However, since inhibition by oxygen will be reduced if the oxygen density in gas is made low, NO<sub>x</sub> can be returned more efficiently and an adsorbent can be reproduced.

[0021] For example, in the case of the adsorbent which generally contains noble metals, when the oxygen density in the negotiation gas at the time of regeneration is below 0.5 %, NO<sub>x</sub> can be most efficiently returned with a hydrocarbon. Moreover, even if it is the case where the oxygen

density in negotiation gas is more than 0.5 %, it is possible to return NOx so efficiently that an oxygen density be low.

[0022] Moreover, NOx may be able to be efficiently returned by reducing the oxygen density in negotiation gas also except the adsorbent containing noble metals.

[0023] There are various approaches among the approaches of reducing the oxygen density in the negotiation gas at the time of adsorbent playback. for example, the approach of burning a hydrocarbon etc. and reducing an oxygen density and PSA — the tank of inert gas, such as an approach using adsorbents, such as law, or nitrogen gas, and carbon dioxide gas, is formed, and there is an approach which is mixed with a hydrocarbon and circulated at the time of adsorbent playback.

[0024] The compound used as a reducing agent by the approach of this invention not only promotes reduction decomposition of NOx on an adsorbent, but promotes desorption of NOx. Therefore, it also becomes possible to reproduce an adsorbent at low temperature more, using said compound as a NOx desorption accelerator from an adsorbent. In this case, although it may be desorbed from an adsorbent, without returning a part of NOx and it is necessary to prepare a NOx reduction process in back wash, it is possible to simplify a reduction process as compared with the case where a desorption accelerator is not used.

[0025]

[Function] By the approach by this invention, in order to reproduce by the gas which contains a reducing agent at the time of playback of the adsorbent of NOx, playback progresses easily. Unlike the case where the resurgent gas which does not contain these components is used, bleedoff of NOx takes place also in a 50–200–degree C comparatively low temperature region. NOx currently adsorbed since this has added the component which has the catalysis which promotes the reaction of NOx and a reducing agent in an adsorbent is N2 by the reaction with the hydrocarbon or alcohols which is reducing agents when it does not only \*\*\*\* but becomes more than the constant temperature which it is on an adsorbent. Since it is decomposed, it is thought that it becomes easy to \*\*\*\*.

[0026] NOx from which it is desorbed by this approach is N2 in the spot. Reduction decomposition is carried out and it hardly contains in exhaust gas. Therefore, although the after-treatment equipment of high concentration NOx from which it is desorbed is needed at the time of playback of the usual NOx adsorbent, by the approach by this invention, it becomes unnecessary.

[0027]

[Example]

(Example 1) The whole drawing 1 flow explains an example of the NOx clearance system which becomes this invention. For the exhaust gas 1 containing low concentration NOx, it is mixed with the ozone compounded by the ozonizer 3 at the oxidation process 2, and a part or all NO(s) are NO2. It oxidizes. The gas which flowed out the oxidation process 2 is emitted into atmospheric air from a ventilating tower 5, after being introduced into an adsorption layer 4 and carrying out adsorption treatment of the NOx.

[0028] Said adsorption layer 4 consists of two or more units, and carries out regeneration which extracts the unit with which NOx adsorbed so much and the adsorption capacity force declined, and is mentioned later.

[0029] Nitrogen 6 is introduced into an adsorbent playback process by the fan 7, and the adsorbent unit 8 extracted from the adsorption layer 4 is circulated. When the oxygen density of the unit 8 interior fully falls, a hydrocarbon 9 is introduced into a nitrogen air current, with heating apparatus 10, it heats at about 200 degrees C, and they is circulated. NOx is N2 by the hydrocarbon on a unit 8. Reduction decomposition is carried out. The gas after decomposition is again introduced into the upstream of an adsorption layer 4. When NOx and the hydrocarbon unreacted in gas after decomposition remain, after adsorption treatment is carried out by the adsorption layer 4, atmospheric-air bleedoff is carried out from a ventilating tower 5. The unit 8 which regeneration ended is again built into an adsorption layer 4.

[0030] It becomes possible to return promptly and to also defang NOx which carried out adsorption treatment of the low-concentration NOx efficiently by this system, and stuck to the

adsorbent.

[0031] (Example 2) The whole drawing 2 flow explains an example of the NO<sub>x</sub> clearance system which becomes this invention. The exhaust gas 1 containing low concentration NO<sub>x</sub> is introduced into an adsorption layer 4, and after adsorption treatment of the NO<sub>x</sub> is carried out here, atmospheric-air bleedoff of it is carried out from a ventilating tower 5. An adsorption layer 4 consists of two or more units, and carries out regeneration which extracts the unit with which NO<sub>x</sub> adsorbed so much and the adsorption capacity force declined, and is mentioned later.

[0032] Nitrogen 6 is introduced into a unit 8 by the fan 7, and it introduces into the upstream of an adsorption layer 4 further. When the oxygen density of the unit 8 interior fully falls, it changes so that the gas which flowed out of the adsorbent unit 8 may circulate through the passage change bulbs 11 and 12 and it may flow into 8 again. The circulation negotiation of the gas heated at about 200 degrees C with heating apparatus 10 is carried out by the fan 7, and 8 is heated to temperature required for reduction decomposition of NO<sub>x</sub>. It is NO<sub>x</sub> from which a hydrocarbon 9 is simultaneously introduced in the circulatory system, and it is desorbed from 8 to desorption and coincidence N<sub>2</sub>. It understands a returned part. Reduction clarification of the NO<sub>x</sub> is fully carried out, and 8 which playback completed is again included in an adsorption layer 4.

[0033] NO<sub>x</sub> can be purified on an adsorbent by being able to carry out the adsorption treatment of the low-concentration NO<sub>x</sub> efficiently by this approach, and performing heating regeneration by the circulatory system to the adsorbent after NO<sub>x</sub> adsorption.

[0034] (Example 3) The nitrogen-oxides adsorbent used by this invention was prepared as follows.

[0035] Oxidization yttrium 23g, 31g of barium oxide, and 16g of copper oxide were kneaded with the RAIKAI machine for 1 hour. After drying a kneading product at 150 degrees C for 2 hours, preliminary baking was carried out at 500 degrees C for 2 hours. After the mortar fully ground the obtained oxide, it calcinated at 870 more degrees C for 4 hours. Next, the obtained powder was pressed in discoid with a diameter of 45mm, this was crushed, and the particle size regulation was carried out to the shape of a grain with a particle size of 0.5-1mm. It turned out that it is the multiple oxide which this compound has the presentation of YBaCuO 7-x, and has the crystal structure of a perovskite mold as a result of X diffraction measurement.

[0036] Above granular YBaCuO 7-x The dinitro diamine platonic acid water solution of the specified quantity was sunk in. After drying this at 150 degrees C for 2 hours, it calcinated at 500 degrees C for 2 hours, and the adsorbent 1 was obtained. Platinum (Pt) was supported 0.1% of the weight to YBaCuO 7-x as a result of the chemical analysis.

[0037] (Example 4) The adsorption engine performance of NO<sub>x</sub> of an adsorbent 1 was measured. The center section of cylinder tubing made from quartz glass with a bore [ of 20mm ] and a die length of 800mm was filled up with 4ml of an adsorbent 1, and NO content gas was processed on condition that a table 1. In addition, the temperature of an adsorbent inserted and measured the thermocouple. Moreover, the inlet port of cylinder tubing made from quartz glass and the NO<sub>x</sub> (NO and NO<sub>2</sub>) concentration in outlet gas carried out continuation measurement with the chemiluminescence type nitrogen-oxides analyzer.

[0038]

[A table 1]



表 1

試験ガス組成	
NO	5 ppm
O <sub>2</sub>	20 %
水蒸気	3 %
N <sub>2</sub>	残 部
空間速度	10000 h <sup>-1</sup>
吸着温度	25 ~ 100 °C

[0039] The NOx elimination factor was computed according to the degree type.

[0040]

[Equation 1]

$$\text{NOx除去率} = \frac{(\text{入口ガス中のNOx}) - (\text{出口ガス中のNOx})}{(\text{入口ガス中のNOx})} \times 100(\%)$$

... (数1)

[0041] NOx is NO and NO2 here. Sum density (ppm) is expressed.

[0042] The rate of NOx adsorption treatment 15 hours after a gas negotiation of the adsorbent 1 set as each temperature is shown in a table 2. It turned out that an adsorbent 1 has the high NOx adsorption engine performance in the temperature region near a room temperature.

[0043]

[A table 2]

表 2

吸着温度	NO除去率
25	97 %
50	95 %
100	68 %

[0044] (Example 5) After circulating NOx content gas at 25 degrees C like the example 4 for 15 hours and performing adsorption treatment using an adsorbent 1, regeneration was performed by the following approaches.

[0045] It was filled up with the nitrogen gas containing a propylene shown in a table 3 in cylinder tubing made from quartz glass filled up with the adsorbent 1 after NOx adsorption treatment, and the other end was made to return and circulate through the gas which flowed out of the end of cylinder tubing using the circulating pump. Cylinder tubing was heated to 200 degrees C, and regeneration was carried out for 30 minutes.

[0046] As a result of extracting the gas in cylinder tubing and measuring NOx concentration after regeneration, it was 0.1 ppm or less. Moreover, although temperature up of the adsorbent 1 after regeneration was carried out to 700 degrees C in the nitrogen air current, desorption of NOx from an adsorbent was not accepted. These results showed most NOx which stuck to the adsorbent 1 by the above-mentioned regeneration having \*\*\*\*ed, and having decomposed into nitrogen.

[0047]

[A table 3]

表 3

試験ガス組成	
プロピレン	1 0 0 0 ppm
N <sub>2</sub>	残 部
空間速度	2 0 0 0 h <sup>-1</sup>
再生温度	2 0 0 ℃

[0048] (Example 6) After circulating NOx content gas at 25 degrees C like the example 4 for 15 hours and performing adsorption treatment using an adsorbent 1, regeneration was performed by the following approaches.

[0049] In cylinder tubing made from quartz glass filled up with said adsorbent 1, as shown in a table 4, it was filled up with the nitrogen which does not contain a reducing agent, and the other end was made to return and circulate through the gas which flowed out of the end of cylinder tubing using the circulating pump. Cylinder tubing was simultaneously heated to 200 degrees C, and regeneration was carried out for 30 minutes.

[0050] the result of having extracted the gas in cylinder tubing and having measured NOx concentration after regeneration -- about 13 ppm it was . Consequently, when hydrocarbon oxygen was not contained in regeneration gas, it turned out that a part or all NOx are desorbed from an adsorbent 1 while fully not having been returned by it.

[0051]

[A table 4]

表 4

試験ガス組成	
N <sub>2</sub>	1 0 0 %
空間速度	2 0 0 0 h <sup>-1</sup>
再生温度	2 0 0 ℃

[0052] (Example 7) The NOx adsorbent used by this invention was prepared as follows.

[0053] Commercial granular gamma-aluminum 2O3 is crushed with a mortar, and it is the particle size of 0.5-1mm. The particle size regulation was carried out to the shape of a grain. The dinitro diamine platinic acid water solution of the specified quantity was sunk into this, and it dried at 150 degrees C for 2 hours. It calcinated at 500 more degrees C for 2 hours, and the adsorbent 2 was obtained. Platinum (Pt) is [ as opposed to / the result of a chemical analysis / aluminum 2O3 ] 0.1. Weight % support of was done.

[0054] (Example 8) Replaced with the dinitro diamine platinic acid water solution in the example 7, and the cobalt nitrate water solution was used, and also the adsorbent 3 was obtained like the example 7. The amount and concentration of a cobalt nitrate water solution were adjusted so that the cobalt contained in an adsorbent 3 might become 10 % of the weight.

[0055] (Example 9) aluminum2O3/SiO2 of marketing After the ratio kneaded the ZSM-5 zeolite powder which is about 30 with the copper-nitrate water solution and mortar of the specified quantity and dried at 150 degrees C for 2 hours, it calcinated at 500 degrees C for 2 hours, and the adsorbent 4 was obtained. The amount and concentration of a copper-nitrate water solution were adjusted so that the copper contained in an adsorbent 4 might become 10 % of the weight.

[0056] (Example 10) The result of having conducted the adsorption experiment of NO on the same conditions as an example 4 in 25 degrees C about adsorbents 2-4 for 15 hours is shown in a table 5. Any adsorbent was found by having high adsorption capacity.

[0057]

[A table 5]  
表 5

吸着剤	NO除去率
吸着剤 2	94%
吸着剤 3	92%
吸着剤 4	98%

[0058] (Example 11) About the adsorbents 2-4 which performed NOx adsorption treatment in the example 10, replaced with the propylene, and ethylene was used, and also the playback experiment of an adsorbent was conducted on the same conditions as an example 5. The gas in cylinder tubing made from quartz glass is extracted after regeneration, and the result of having measured NOx concentration is shown in a table 6. When NOx which stuck to any adsorbent \*\*\*\*ed, it turned out that it decomposes simultaneously and is changed into nitrogen.

[0059]

[A table 6]

表 6

吸着剤	再生処理後ガス中の NO濃度
吸着剤 2	0.2 ppm
吸着剤 3	0.2 ppm
吸着剤 4	0.1 ppm

[0060] (Example 12) The playback experiment of an adsorbent was conducted on the same conditions as an example 5 except having replaced with the propylene, having replaced with nitrogen using ethyl alcohol, and having used air about the adsorbents 2-4 which performed NOx adsorption treatment in the example 10. The gas in cylinder tubing made from quartz glass is extracted after regeneration, and the result of having measured NOx concentration is shown in a table 7. When NOx which stuck to any adsorbent \*\*\*\*ed, it turned out that it decomposes simultaneously and is changed into nitrogen.

[0061]

[A table 7]

表 7

吸着剤	再生処理後ガス中の NO濃度
吸着剤 2	0.3 ppm
吸着剤 3	0.4 ppm
吸着剤 4	0.2 ppm

[0062] (Example 13) About an adsorbent 1, it replaces with NO in 25 degrees C, and is NO2. The result to which predetermined carried out time amount operation of the adsorption experiment of NO on the same conditions as an example 4 is shown in a table 8 except having used it. An adsorbent 1 is high NO2. It turned out that it has adsorption capacity.

[0063]

[A table 8]

表 8

吸着時間 (h r)	NO 除去率
1 5	9 8 %
4 8	9 5 %
9 6	8 8 %

[0064] (Example 14) At an example 13, it is NO<sub>2</sub>. About the adsorbent 1 which performed adsorption treatment at 25 degrees C for 15 hours, the playback experiment on the same conditions as an example 5 was conducted. As a result of extracting the gas in cylinder tubing made from quartz glass and measuring NO<sub>x</sub> concentration after regeneration, it was about 0.2 ppm. Moreover, although temperature up of the adsorbent 1 after regeneration was carried out to 700 degrees C in the nitrogen air current, the desorption from the adsorbent of NO<sub>x</sub> was not accepted. From this result, it is NO<sub>2</sub>. The adsorbent to which it stuck can also be regenerated by the approach of this invention, and it is NO<sub>2</sub>. It turned out that reduction clarification can be carried out on an adsorbent like NO.

[0065] (Example 15) The playback experiment was conducted using the adsorbent 4 to which NO was made to stick in an example 10.

[0066] It was filled up with the gas of the presentation shown in a table 9 in cylinder tubing made from quartz glass filled up with the adsorbent 4 after adsorption treatment, and the other end was made to return and circulate through the gas which flowed out of the end of cylinder tubing using the circulating pump. Cylinder tubing was heated to 200 degrees C, and regeneration was carried out for 30 minutes.

[0067] The urea used as a reducing agent was kept as a water solution, and after it trickled the specified quantity in quartz-glass tubing for urea decomposition heated at 400 degrees C and hydrolyzed, it was mixed with other gas constituents.

[0068] As a result of extracting the gas in cylinder tubing and measuring NO<sub>x</sub> concentration after regeneration, it was 0.1 ppm or less. This result showed that a urea was used for a reducing agent and the reduction clarification of the NO could be carried out on an adsorbent.

[0069]

[A table 9]

表 9

試験ガス組成	
尿 素	5 0 0 ppm
水 蒸 気	3 %
O <sub>2</sub>	2 0 %
N <sub>2</sub>	残 部
空間速度	2 0 0 0 h <sup>-1</sup>
再生温度	2 0 0 ℃

[0070]

[Effect of the Invention] Since according to this invention it is not necessary to prepare a catalyst bed other than an adsorbent in case clarification processing of the low concentration NO<sub>x</sub> is carried out, a compact and efficient clarification processing can be performed and it is especially suitable for exhaust gas denitrification of an automobile tunnel, a basement car park, etc.

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TECHNICAL FIELD

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[Industrial Application] This invention relates to the processing system of the low concentration NOx content gas which removes efficiently low-concentration NOx especially contained in the tunnel for automobiles, a subway way, ventilation gas, etc. from an inside-of-a-house motor pool, and its art about the clearance approach of the nitrogen oxides (NOx) contained in atmospheric air.

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PRIOR ART

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[Description of the Prior Art] Generally as the defanging clearance approach of NOx in exhaust gas, ammonia is added to NOx content exhaust gas in a thermal power station, and it is N2 [ harmless on a catalyst ]. The selective catalytic reduction process to decompose is mainly applied, and the approach of on the other hand understanding NOx a returned part on a three way component catalyst in a gasoline engine vehicle is applied.

[0003] Therefore, ammonia is added in the high-concentration NOx content gas heated as an art of thin NOx in atmospheric air after condensing NOx with an adsorbent beforehand, and it is harmless N2 with a selective catalytic reduction process. The approach (JP,5-78369,B) of decomposing and emitting etc. is proposed.

[0004] on the other hand -- the gestalt of NOx -- NO2 it is -- if -- since the clearance by the adsorbent of NOx or the absorption clearance by alkali is comparatively easy also under moisture coexistence It is NO in low-concentration NOx content gas by addition of corona discharge or ozone NO2 It oxidizes and is this NO2. It is [ the approach of carrying out absorption clearance by the alkaline lean solution, and ] NO by ozonate NO2 It oxidizes and is this NO2. The approach of carrying out adsorption treatment etc. is proposed (JP,6-99030,A).

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**EFFECT OF THE INVENTION**

---

[Effect of the Invention] Since according to this invention it is not necessary to prepare a catalyst bed other than an adsorbent in case clarification processing of the low concentration NOx is carried out, a compact and efficient clarification processing can be performed and it is especially suitable for exhaust gas denitrification of an automobile tunnel, a basement car park, etc.

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[Translation done.]



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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] This invention is the approach of removing efficiently low-concentration NO<sub>x</sub> which solves the fault of the above-mentioned conventional technique and is contained in the tunnel for automobiles, a subway way, ventilation gas, etc. from an inside-of-a-house motor pool.

[0006] Each conventional technique is the approach which was economical and was excellent, when reaction temperature is usually 200 degrees C or more and processes hot exhaust gas, but adaptation is difficult when [ of ordinary temperature like tunnel ventilation gas ] processing the gas of a large quantity moreover. therefore, as an art of thin NO<sub>x</sub> in atmospheric air Ammonia is added in the high-concentration NO<sub>x</sub> content gas heated after condensing NO<sub>x</sub> with an adsorbent beforehand, and it is harmless N<sub>2</sub> with a selective catalytic reduction process. By the approach of decomposing and emitting 90% or more of NO<sub>x</sub> generally discharged in these atmospheric air is NO lacking in adsorbent, and since the adsorption engine performance of NO will get extremely bad if moisture moreover contains in raw gas, it is usually necessary to dehumidify it beforehand from raw gas. Therefore, a desiccant is needed besides a NO<sub>x</sub> adsorbent and there is a trouble of causing processing cost lifting.

[0007] furthermore, the gestalt of NO<sub>x</sub> -- NO<sub>2</sub> it is -- if, since the clearance by the adsorbent of NO<sub>x</sub> or the absorption clearance by alkali is comparatively easy also under moisture coexistence It is [ the approach of oxidizing NO in low-concentration NO<sub>x</sub> content gas to NO<sub>2</sub> by addition of corona discharge or ozone, and carrying out absorption clearance of this NO<sub>2</sub> by the alkaline lean solution, and ] NO by ozonate NO<sub>2</sub> It oxidizes and is this NO<sub>2</sub>. Although there is the approach of carrying out adsorption treatment etc. By these approaches, there is a trouble of consuming a lot of power as energy for oxidizing NO to NO<sub>2</sub>. Anyway, playback of an adsorbent is needed, when the adsorption capacity force of NO<sub>x</sub> by the adsorbent is saturated with the removal method of the low concentration NO<sub>x</sub> by the adsorbent and it stops showing predetermined NO<sub>x</sub> clearance effectiveness. Usually, this playback is performed by heating resurgent gas with a sink to an adsorbent. Therefore, the great energy for heating is needed for playback of an adsorbent, and it is not economical. High-concentration NO<sub>x</sub> will contain in the resurgent gas which let the adsorbent pass, temperature up is further carried out to predetermined temperature if needed, a reducing agent is added, and it is N<sub>2</sub> [ harmless on a denitrification catalyst ]. In decomposing and emitting \*\*\*\*, it is NO<sub>2</sub>. A case will be absorbed with an alkali solution. for this reason -- new -- a denitrification catalyst -- a column may be required Usually, ammonia and hydrocarbons are proposed by the reducing agent of this denitrification reaction.

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**EXAMPLE**

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**[Example]**

(Example 1) The whole drawing 1 flow explains an example of the NOx clearance system which becomes this invention. For the exhaust gas 1 containing low concentration NOx, it is mixed with the ozone compounded by the ozonizer 3 at the oxidation process 2, and a part or all NO(s) are NO2. It oxidizes. The gas which flowed out the oxidation process 2 is emitted into atmospheric air from a ventilating tower 5, after being introduced into an adsorption layer 4 and carrying out adsorption treatment of the NOx.

[0028] Said adsorption layer 4 consists of two or more units, and carries out regeneration which extracts the unit with which NOx adsorbed so much and the adsorption capacity force declined, and is mentioned later.

[0029] Nitrogen 6 is introduced into an adsorbent playback process by the fan 7, and the adsorbent unit 8 extracted from the adsorption layer 4 is circulated. When the oxygen density of the unit 8 interior fully falls, a hydrocarbon 9 is introduced into a nitrogen air current, with heating apparatus 10, it heats at about 200 degrees C, and they is circulated. NOx is N2 by the hydrocarbon on a unit 8. Reduction decomposition is carried out. The gas after decomposition is again introduced into the upstream of an adsorption layer 4. When NOx and the hydrocarbon unreacted in gas after decomposition remain, after adsorption treatment is carried out by the adsorption layer 4, atmospheric-air bleedoff is carried out from a ventilating tower 5. The unit 8 which regeneration ended is again built into an adsorption layer 4.

[0030] It becomes possible to return promptly and to also defang NOx which carried out adsorption treatment of the low-concentration NOx efficiently by this system, and stuck to the adsorbent.

[0031] (Example 2) The whole drawing 2 flow explains an example of the NOx clearance system which becomes this invention. The exhaust gas 1 containing low concentration NOx is introduced into an adsorption layer 4, and after adsorption treatment of the NOx is carried out here, atmospheric-air bleedoff of it is carried out from a ventilating tower 5. An adsorption layer 4 consists of two or more units, and carries out regeneration which extracts the unit with which NOx adsorbed so much and the adsorption capacity force declined, and is mentioned later.

[0032] Nitrogen 6 is introduced into a unit 8 by the fan 7, and it introduces into the upstream of an adsorption layer 4 further. When the oxygen density of the unit 8 interior fully falls, it changes so that the gas which flowed out of the adsorbent unit 8 may circulate through the passage change bulbs 11 and 12 and it may flow into 8 again. The circulation negotiation of the gas heated at about 200 degrees C with heating apparatus 10 is carried out by the fan 7, and 8 is heated to temperature required for reduction decomposition of NOx. It is NOx from which a hydrocarbon 9 is simultaneously introduced in the circulatory system, and it is desorbed from 8 to desorption and coincidence N2. It understands a returned part. Reduction clarification of the NOx is fully carried out, and 8 which playback completed is again included in an adsorption layer 4.

[0033] NOx can be purified on an adsorbent by being able to carry out the adsorption treatment of the low-concentration NOx efficiently by this approach, and performing heating regeneration by the circulatory system to the adsorbent after NOx adsorption.

[0034] (Example 3) The nitrogen-oxides adsorbent used by this invention was prepared as follows.

[0035] Oxidization yttrium 23g, 31g of barium oxide, and 16g of copper oxide were kneaded with the RAIKAI machine for 1 hour. After drying a kneading product at 150 degrees C for 2 hours, preliminary baking was carried out at 500 degrees C for 2 hours. After the mortar fully ground the obtained oxide, it calcinated at 870 more degrees C for 4 hours. Next, the obtained powder was pressed in discoid with a diameter of 45mm, this was crushed, and the particle size regulation was carried out to the shape of a grain with a particle size of 0.5-1mm. It turned out that it is the multiple oxide which this compound has the presentation of YBaCuO 7-x, and has the crystal structure of a perovskite mold as a result of X diffraction measurement.

[0036] Above granular YBaCuO 7-x The dinitro diamine platonic acid water solution of the specified quantity was sunk in. After drying this at 150 degrees C for 2 hours, it calcinated at 500 degrees C for 2 hours, and the adsorbent 1 was obtained. Platinum (Pt) was supported 0.1% of the weight to YBaCuO 7-x as a result of the chemical analysis.

[0037] (Example 4) The adsorption engine performance of NOx of an adsorbent 1 was measured. The center section of cylinder tubing made from quartz glass with a bore [ of 20mm ] and a die length of 800mm was filled up with 4ml of an adsorbent 1, and NO content gas was processed on condition that a table 1. In addition, the temperature of an adsorbent inserted and measured the thermocouple. Moreover, the inlet port of cylinder tubing made from quartz glass and the NOx (NO and NO2) concentration in outlet gas carried out continuation measurement with the chemiluminescence type nitrogen-oxides analyzer.

[0038]

[A table 1]

表 1

試験ガス組成	
NO	5 ppm
O <sub>2</sub>	20 %
水蒸気	3 %
N <sub>2</sub>	残部
空間速度	10000 h <sup>-1</sup>
吸着温度	25 ~ 100 °C

[0039] The NOx elimination factor was computed according to the degree type.

[0040]

[Equation 1]

$$\text{NOx除去率} = \frac{(\text{入口ガス中のNOx}) - (\text{出口ガス中のNOx})}{(\text{入口ガス中のNOx})} \times 100(\%)$$

... (数1)

[0041] NOx is NO and NO2 here. Sum density (ppm) is expressed.

[0042] The rate of NOx adsorption treatment 15 hours after a gas negotiation of the adsorbent 1 set as each temperature is shown in a table 2. It turned out that an adsorbent 1 has the high NOx adsorption engine performance in the temperature region near a room temperature.

[0043]

[A table 2]

表 2

吸着温度	NO除去率
25	97%
50	95%
100	68%

[0044] (Example 5) After circulating NOx content gas at 25 degrees C like the example 4 for 15 hours and performing adsorption treatment using an adsorbent 1, regeneration was performed by the following approaches.

[0045] It was filled up with the nitrogen gas containing a propylene shown in a table 3 in cylinder tubing made from quartz glass filled up with the adsorbent 1 after NOx adsorption treatment, and the other end was made to return and circulate through the gas which flowed out of the end of cylinder tubing using the circulating pump. Cylinder tubing was heated to 200 degrees C, and regeneration was carried out for 30 minutes.

[0046] As a result of extracting the gas in cylinder tubing and measuring NOx concentration after regeneration, it was 0.1 ppm or less. Moreover, although temperature up of the adsorbent 1 after regeneration was carried out to 700 degrees C in the nitrogen air current, desorption of NOx from an adsorbent was not accepted. These results showed most NOx which stuck to the adsorbent 1 by the above-mentioned regeneration having \*\*\*\*\*ed, and having decomposed into nitrogen.

[0047]

[A table 3]

表 3

試験ガス組成	
プロピレン	1000ppm
N <sub>2</sub>	残部
空間速度	2000h <sup>-1</sup>
再生温度	200℃

[0048] (Example 6) After circulating NOx content gas at 25 degrees C like the example 4 for 15 hours and performing adsorption treatment using an adsorbent 1, regeneration was performed by the following approaches.

[0049] In cylinder tubing made from quartz glass filled up with said adsorbent 1, as shown in a table 4, it was filled up with the nitrogen which does not contain a reducing agent, and the other end was made to return and circulate through the gas which flowed out of the end of cylinder tubing using the circulating pump. Cylinder tubing was simultaneously heated to 200 degrees C, and regeneration was carried out for 30 minutes.

[0050] the result of having extracted the gas in cylinder tubing and having measured NOx concentration after regeneration — about 13 ppm it was . Consequently, when hydrocarbon oxygen was not contained in regeneration gas, it turned out that a part or all NOx are desorbed from an adsorbent 1 while fully not having been returned by it.

[0051]

[A table 4]

表 4

試験ガス組成	
N <sub>2</sub>	100%
空間速度	2000h <sup>-1</sup>
再生温度	200℃

[0052] (Example 7) The NO<sub>x</sub> adsorbent used by this invention was prepared as follows.

[0053] Commercial granular gamma-aluminum 2O<sub>3</sub> is crushed with a mortar, and it is the particle size of 0.5–1mm. The particle size regulation was carried out to the shape of a grain. The dinitro diamine platonic acid water solution of the specified quantity was sunk into this, and it dried at 150 degrees C for 2 hours. It calcinated at 500 more degrees C for 2 hours, and the adsorbent 2 was obtained. Platinum (Pt) is [ as opposed to / the result of a chemical analysis / aluminum 2O<sub>3</sub> ] 0.1. Weight % support of was done.

[0054] (Example 8) Replaced with the dinitro diamine platonic acid water solution in the example 7, and the cobalt nitrate water solution was used, and also the adsorbent 3 was obtained like the example 7. The amount and concentration of a cobalt nitrate water solution were adjusted so that the cobalt contained in an adsorbent 3 might become 10 % of the weight.

[0055] (Example 9) aluminum2O<sub>3</sub>/SiO<sub>2</sub> of marketing After the ratio kneaded the ZSM-5 zeolite powder which is about 30 with the copper-nitrate water solution and mortar of the specified quantity and dried at 150 degrees C for 2 hours, it calcinated at 500 degrees C for 2 hours, and the adsorbent 4 was obtained. The amount and concentration of a copper-nitrate water solution were adjusted so that the copper contained in an adsorbent 4 might become 10 % of the weight.

[0056] (Example 10) The result of having conducted the adsorption experiment of NO on the same conditions as an example 4 in 25 degrees C about adsorbents 2–4 for 15 hours is shown in a table 5. Any adsorbent was found by having high adsorption capacity.

[0057]

[A table 5]

表 5

吸着剤	NO除去率
吸着剤 2	94%
吸着剤 3	92%
吸着剤 4	98%

[0058] (Example 11) About the adsorbents 2–4 which performed NO<sub>x</sub> adsorption treatment in the example 10, replaced with the propylene, and ethylene was used, and also the playback experiment of an adsorbent was conducted on the same conditions as an example 5. The gas in cylinder tubing made from quartz glass is extracted after regeneration, and the result of having measured NO<sub>x</sub> concentration is shown in a table 6. When NO<sub>x</sub> which stuck to any adsorbent \*\*\*\*\*ed, it turned out that it decomposes simultaneously and is changed into nitrogen.

[0059]

[A table 6]

表 6

吸着剤	再生処理後ガス中の NO濃度
吸着剤 2	0.2 ppm
吸着剤 3	0.2 ppm
吸着剤 4	0.1 ppm

[0060] (Example 12) The playback experiment of an adsorbent was conducted on the same conditions as an example 5 except having replaced with the propylene, having replaced with nitrogen using ethyl alcohol, and having used air about the adsorbents 2-4 which performed NOx adsorption treatment in the example 10. The gas in cylinder tubing made from quartz glass is extracted after regeneration, and the result of having measured NOx concentration is shown in a table 7. When NOx which stuck to any adsorbent \*\*\*\*ed, it turned out that it decomposes simultaneously and is changed into nitrogen.

[0061]

[A table 7]

表 7

吸着剤	再生処理後ガス中の NO濃度
吸着剤 2	0.3 ppm
吸着剤 3	0.4 ppm
吸着剤 4	0.2 ppm

[0062] (Example 13) About an adsorbent 1, it replaces with NO in 25 degrees C, and is NO2. The result to which predetermined carried out time amount operation of the adsorption experiment of NO on the same conditions as an example 4 is shown in a table 8 except having used it. An adsorbent 1 is high NO2. It turned out that it has adsorption capacity.

[0063]

[A table 8]

表 8

吸着時間 (h r)	NO除去率
1 5	9 8 %
4 8	9 5 %
9 6	8 8 %

[0064] (Example 14) At an example 13, it is NO2. About the adsorbent 1 which performed adsorption treatment at 25 degrees C for 15 hours, the playback experiment on the same conditions as an example 5 was conducted. As a result of extracting the gas in cylinder tubing made from quartz glass and measuring NOx concentration after regeneration, it was about 0.2 ppm. Moreover, although temperature up of the adsorbent 1 after regeneration was carried out to 700 degrees C in the nitrogen air current, the desorption from the adsorbent of NOx was not accepted. From this result, it is NO2. The adsorbent to which it stuck can also be regenerated by the approach of this invention, and it is NO2. It turned out that reduction clarification can be carried out on an adsorbent like NO.

[0065] (Example 15) The playback experiment was conducted using the adsorbent 4 to which NO

was made to stick in an example 10.

[0066] It was filled up with the gas of the presentation shown in a table 9 in cylinder tubing made from quartz glass filled up with the adsorbent 4 after adsorption treatment, and the other end was made to return and circulate through the gas which flowed out of the end of cylinder tubing using the circulating pump. Cylinder tubing was heated to 200 degrees C, and regeneration was carried out for 30 minutes.

[0067] The urea used as a reducing agent was kept as a water solution, and after it trickled the specified quantity in quartz-glass tubing for urea decomposition heated at 400 degrees C and hydrolyzed, it was mixed with other gas constituents.

[0068] As a result of extracting the gas in cylinder tubing and measuring NOx concentration after regeneration, it was 0.1 ppm or less. This result showed that a urea was used for a reducing agent and the reduction clarification of the NO could be carried out on an adsorbent.

[0069]

[A table 9]

表 9

試験ガス組成	
尿 素	5 0 0 ppm
水 蒸 気	3 %
O <sub>2</sub>	2 0 %
N <sub>2</sub>	残 部
空間速度	2 0 0 0 h <sup>-1</sup>
再生温度	2 0 0 ℃

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] It is the conceptual diagram of the equipment used for processing of the low concentration NOx content gas which becomes this invention.

[Drawing 2] It is the conceptual diagram of the equipment used for processing of the low concentration NOx content gas which becomes this invention.

[Description of Notations]

1 [ -- An adsorption layer, 5 / -- A ventilating tower, 6 / -- Nitrogen, 7 / -- A fan, 8 / -- The adsorbent unit, 9 which were extracted from the adsorption layer 4 / -- A hydrocarbon, 10 / -- 11 Heating apparatus, 12 / -- Passage change bulb. ] -- The exhaust gas, 2 containing low concentration NOx -- An oxidation process, 3 -- An ozonizer, 4

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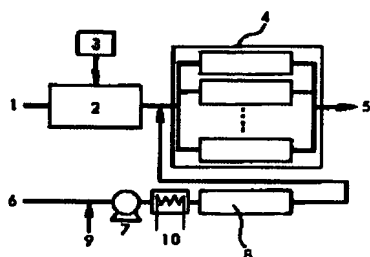
2.\*\*\* shows the word which can not be translated.

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## DRAWINGS

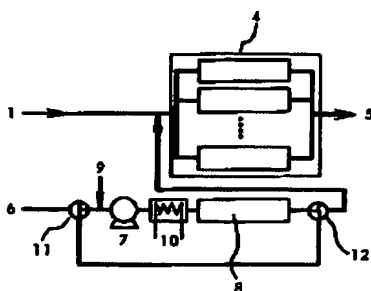
[Drawing 1]

図 1



[Drawing 2]

図 2



[Translation done.]

(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号

特開平8-257351

(43)公開日 平成8年(1996)10月8日

(51)Int.Cl. <sup>6</sup>	識別記号	庁内整理番号	F I	技術表示箇所
B 0 1 D 53/56			B 0 1 D 53/34	1 2 9 B
53/34	Z A B			Z A B
53/81				1 2 9 A

審査請求 未請求 請求項の数12 O L (全 8 頁)

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最終頁に続く

(54)【発明の名称】 低濃度NO<sub>x</sub>含有ガスの処理システム及びその処理方法

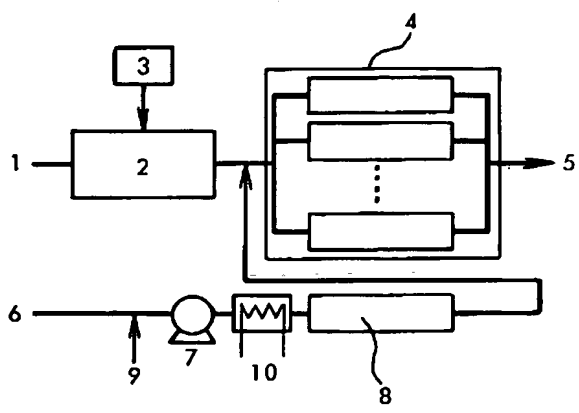
(57)【要約】

【目的】本発明は、自動車用トンネル、地下道路や屋内自動車駐車場からの換気ガス等に含まれる低濃度のNO<sub>x</sub>を吸着剤を用いて除去する際に、NO<sub>x</sub>吸着後の吸着剤を効率良く再生し、かつ吸着剤に吸着したNO<sub>x</sub>を無害化することを目的とする。

【構成】本発明による低濃度のNO<sub>x</sub>を効率良く除去する方法では、吸着剤がNO<sub>x</sub>分解触媒能を有し、NO<sub>x</sub>吸着後の吸着剤の再生を尿素、炭化水素あるいはアルコール類等の還元剤を含有するガスを流通させることによって行うことを特徴とする。

【効果】本発明の方法により、NO<sub>x</sub>吸着剤の再生時に新たにNO<sub>x</sub>浄化触媒を設けることなく、吸着剤上でNO<sub>x</sub>を浄化し無害化することができる。

図 1



(2)

特開平8-257351

1

## 【特許請求の範囲】

【請求項1】排ガス中のダスト成分を除去する除塵装置と、NO<sub>x</sub>を吸着除去する吸着装置と、該吸着装置の再生時には還元剤を供給して、捕集されたNO<sub>x</sub>を脱着時に該吸着装置内で窒素に還元分解する制御装置とを有することを特徴とする低濃度NO<sub>x</sub>含有ガスの処理システム。

【請求項2】排ガス中のダスト成分を除塵装置で除去した後、NO酸化装置で排ガス中のNOの一部または全部をNO<sub>2</sub>に酸化し、吸着装置でNO<sub>x</sub>を吸着除去し、該吸着装置の再生時には還元剤を供給して、捕集されたNO<sub>x</sub>を脱着時に該吸着装置内で窒素に還元分解することを特徴とする低濃度NO<sub>x</sub>含有ガスの処理システム。

【請求項3】排ガス中のダスト成分を除塵装置で除去した後、NO酸化装置で排ガス中のNOの一部または全部をNO<sub>2</sub>に酸化し、吸着装置でNO<sub>x</sub>を吸着除去し、該吸着装置の再生時には還元剤を含むガスを供給して捕集されたNO<sub>x</sub>を脱着させ、その一部を該吸着装置内で窒素に還元分解した後NO<sub>x</sub>還元装置に導入し、該NO<sub>x</sub>還元装置で前記脱着NO<sub>x</sub>の残部を還元浄化することを特徴とする低濃度NO<sub>x</sub>含有ガスの処理システム。

【請求項4】低濃度NO<sub>x</sub>含有ガスを吸着剤に接触させ、NO<sub>x</sub>を吸着除去するシステムにおいて、吸着剤の再生時に該吸着剤を流通するガス中の酸素濃度を低減する装置を設け、該装置により含有酸素濃度を低減し、かつ炭化水素あるいはアルコール類を含有するガスを流通させ、吸着剤上でNO<sub>x</sub>をN<sub>2</sub>に還元分解することを特徴とする低濃度NO<sub>x</sub>含有ガスの処理システム。

【請求項5】請求項4記載の低濃度NO<sub>x</sub>含有ガスの処理システムにおいて、吸着剤の再生時に炭化水素あるいはアルコール類を含有する不活性ガスを流通させ、吸着剤上でNO<sub>x</sub>をN<sub>2</sub>に還元分解することを特徴とする低濃度NO<sub>x</sub>含有ガスの処理システム。

【請求項6】低濃度NO<sub>x</sub>含有ガスを吸着剤に接触させ、NO<sub>x</sub>を吸着除去する方法において、吸着剤の再生時には還元剤を含有するガスを流通させ、吸着剤上でNO<sub>x</sub>をN<sub>2</sub>に還元分解することを特徴とする低濃度NO<sub>x</sub>含有ガスの処理方法。

【請求項7】請求項6記載の低濃度NO<sub>x</sub>含有ガスの処理方法において、還元剤が炭化水素あるいはアルコール類であることを特徴とする低濃度NO<sub>x</sub>含有ガスの処理方法。

【請求項8】請求項6記載の低濃度NO<sub>x</sub>含有ガスの処理方法において、還元剤が尿素あるいは尿素の分解生成物であることを特徴とする低濃度NO<sub>x</sub>含有ガスの処理方法。

【請求項9】請求項6記載の低濃度NO<sub>x</sub>含有ガスの処理方法において、吸着剤再生時の吸着剤充填層の温度を100℃～500℃に調整して再生を行うことを特徴とする低濃度NO<sub>x</sub>含有ガスの処理方法。

2

【請求項10】請求項6記載の低濃度NO<sub>x</sub>含有ガスの処理方法において、吸着剤がNO<sub>x</sub>と還元剤との反応に対して触媒作用を有することを特徴とする低濃度NO<sub>x</sub>含有ガスの処理方法。

【請求項11】低濃度NO<sub>x</sub>含有ガスを吸着剤に接触させ、NO<sub>x</sub>を吸着除去する方法において、吸着剤の再生時には還元剤を含有するガスを流通させ、吸着剤上で一部のNO<sub>x</sub>をN<sub>2</sub>に還元分解し、かつ吸着剤の後流にNO<sub>x</sub>還元分解工程を設けたことを特徴とする低濃度NO<sub>x</sub>含有ガスの処理方法。

【請求項12】低濃度NO<sub>x</sub>含有ガスを吸着剤に接触させ、NO<sub>x</sub>を吸着除去する方法において、吸着剤の再生時にはNO<sub>x</sub>の脱離を促進する化合物を含有するガスを流通させ、吸着剤よりNO<sub>x</sub>を脱離させた後、後流に設けたNO<sub>x</sub>還元分解工程でN<sub>2</sub>に還元分解することを特徴とする低濃度NO<sub>x</sub>含有ガスの処理方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は大気中に含まれる窒素酸化物(NO<sub>x</sub>)の除去方法に関し、特に自動車用トンネル、地下道路や屋内自動車駐車場からの換気ガス等に含まれる低濃度のNO<sub>x</sub>を効率良く除去する低濃度NO<sub>x</sub>含有ガスの処理システム及びその処理方法に関する。

## 【0002】

【従来の技術】一般に排ガス中のNO<sub>x</sub>の無害化除去方法としては、火力発電所においてはNO<sub>x</sub>含有排ガスにアンモニアを添加し、触媒上で無害なN<sub>2</sub>に分解する選択接触還元法が主に適用されており、一方ガソリンエンジン車においては三元触媒上でNO<sub>x</sub>を還元分解する方法が適用されている。

【0003】そのため大気中の稀薄なNO<sub>x</sub>の処理方法としては、予め吸着剤によりNO<sub>x</sub>を濃縮した後、加熱された高濃度のNO<sub>x</sub>含有ガスにアンモニアを添加し選択接触還元法で無害なN<sub>2</sub>に分解して放出する方法(特公平5-78369号)などが提案されている。

【0004】一方、NO<sub>x</sub>の形態がNO<sub>2</sub>であれば、水分共存下でもNO<sub>x</sub>の吸着剤による除去あるいはアルカリによる吸収除去は比較的容易なので、低濃度のNO<sub>x</sub>含有ガス中のNOをコロナ放電やオゾンの添加によりNO<sub>2</sub>に酸化し、該NO<sub>2</sub>をアルカリ性吸収液で吸収除去する方法や、NOをオゾン酸化によりNO<sub>2</sub>に酸化し、該NO<sub>2</sub>を吸着除去する方法などが提案されている(特開平6-99030号)。

## 【0005】

【発明が解決しようとする課題】本発明は上記した従来技術の欠点を解決し、自動車用トンネル、地下道路や屋内自動車駐車場からの換気ガス等に含まれる低濃度のNO<sub>x</sub>を効率良く除去する方法である。

【0006】従来技術はいずれも反応温度が通常200℃以上であり、高温の排ガスを処理する場合には経済的

(3)

特開平8-257351

3

で優れた方法であるが、トンネル換気ガスのような常温のしかも大量のガスを処理する場合には適応が難しい。そのため大気中の稀薄なNO<sub>x</sub>の処理方法としては、予め吸着剤によりNO<sub>x</sub>を濃縮した後、加熱された高濃度のNO<sub>x</sub>含有ガスにアンモニアを添加し選択接触還元法で無害なN<sub>2</sub>に分解して放出する方法では、一般にこれら大気中に排出されたNO<sub>x</sub>の90%以上は吸着性に乏しいNOであり、しかも処理ガス中に水分が含有されるとNOの吸着性能が極端に悪くなるため、通常処理ガスから予め除湿する必要がある。そのためNO<sub>x</sub>吸着剤以外にも脱湿剤が必要になり、処理コスト上昇を招くという問題点がある。

【0007】さらに、NO<sub>x</sub>の形態がNO<sub>2</sub>であれば、水分共存下でもNO<sub>x</sub>の吸着剤による除去あるいはアルカリによる吸収除去は比較的容易なので、低濃度のNO<sub>x</sub>含有ガス中のNOをコロナ放電やオゾンの添加によりNO<sub>2</sub>に酸化し、該NO<sub>2</sub>をアルカリ性吸収液で吸収除去する方法や、NOをオゾン酸化によりNO<sub>2</sub>に酸化し、該NO<sub>2</sub>を吸着除去する方法などがあるが、これらの方法では、NOをNO<sub>2</sub>に酸化するためのエネルギーとして多量の電力を消費するという問題点がある。いずれにしても、吸着剤による低濃度NO<sub>x</sub>の除去法では吸着剤によるNO<sub>x</sub>の吸着能力が飽和し所定のNO<sub>x</sub>除去効率を示さなくなった場合には、吸着剤の再生が必要となる。通常、この再生は吸着剤に再生ガスを流しながら加熱することにより行われる。従って吸着剤の再生には加熱のための多大なエネルギーが必要となり、経済的でない。吸着剤を通した再生ガスには高濃度のNO<sub>x</sub>が含有されることになり、さらに必要に応じ所定温度に昇温して還元剤を添加し、脱硝触媒上で無害なN<sub>2</sub>に分解して放出したり、NO<sub>2</sub>の場合はアルカリ溶液で吸収することになる。このため、新たに脱硝触媒塔が必要な場合もある。通常この脱硝反応の還元剤にはアンモニアや炭化水素類が提案されている。

【0008】

【課題を解決するための手段】上記問題点は下記的手段によって達成できる。本発明による低濃度のNO<sub>x</sub>を効率良く除去する処理システム及びその処理方法では、吸着剤の再生を還元剤を含有するガスを流通させることによって行うことを特徴とする。通常、吸着剤により除去されたNO<sub>x</sub>は、吸着剤の加熱再生により濃縮ガスとして脱離させ、還元分解工程でN<sub>2</sub>に還元分解する。還元分解工程には、濃縮NO<sub>x</sub>含有ガスに還元剤を添加した後触媒上で分解する方法や、アルカリ化合物や溶液に吸収させた後、還元処理する方法などが提案されている。これらの還元分解工程は本発明の方法を適用することで、省略あるいは簡素化することが可能である。

【0009】また、本発明による低濃度のNO<sub>x</sub>を含有する排ガスの処理システムは、吸着装置によりNO<sub>x</sub>を吸着除去し、該吸着装置の再生時には吸着NO<sub>x</sub>を、脱

4

着と同時に該吸着装置内で窒素に還元分解することを特徴とする。吸着装置の性能をさらに向上させるため、吸着装置の上流にNO酸化装置を設置し、排ガス中のNOの一部または全てをNO<sub>2</sub>に酸化しても良い。また、排ガス中にダスト成分が多く含まれる場合には、吸着装置の上流に除塵装置を設けても良い。本システムのNO<sub>x</sub>除去性能を更に向上させるため、吸着装置の下流にNO<sub>x</sub>還元分解装置を設けても良い。

【0010】本発明の低濃度のNO<sub>x</sub>処理方法は用いる還元剤種により2通りに大別できる。一つの方法は還元剤に尿素あるいは尿素の分解生成物を用いる方法であり、もう一つの方法は炭化水素あるいはアルコール類を用いる方法である。

【0011】本発明者等の詳細な検討によれば、再生ガス中にNO<sub>x</sub>の還元剤として作用する化合物が含有されると、速やかに吸着剤の再生が行われることが分かった。しかも通常の再生では、再生時に吸着剤から放出されるガス中には高濃度のNO<sub>x</sub>が含有されるが、本発明の方法では再生時に大部分のNO<sub>x</sub>が、脱離促進剤でもある還元剤により還元除去されるという特徴がある。

【0012】本発明に用いる吸着剤としてはNO<sub>x</sub>吸着能以外に、脱離時に尿素、尿素の分解生成物、炭化水素、あるいはアルコール類とNO<sub>x</sub>との反応促進作用を持つことが特徴である。例えば、アルミナ、シリカ、チタニア、シリカーアルミナ、ゼオライト、活性炭などNO<sub>x</sub>吸着能をもつ各種の物質に還元剤とNO<sub>x</sub>との反応促進作用を持つ各種の物質を添加したものが使用される。これらの代表的なものとしては、還元剤に尿素、あるいは尿素の分解生成物を用いる場合にはPt, Rh, Ru等の貴金属類、V, Mo, W, Cr, Mn, Fe, Co, Ni, Ceなどの卑金属があげられる。また、還元剤に炭化水素あるいはアルコール類を用いる場合にはPt, Rh, Pd, Ru, Au, Ag等の貴金属類、Co, Ni, Fe, Cu, Mn, Gaなどの卑金属があげられる。

【0013】また、NO<sub>x</sub>の吸着能を向上させるために、各種のアルカリ、アルカリ土類、希土類を添加するのも好ましい方法である。たとえばLi, Na, K, Mg, Ca, Sr, Ba, La, Ce等である。

【0014】さらに、NO酸化性能を持つ触媒成分を含有させると、NOをより吸着しやすいNO<sub>2</sub>に変換し吸着することができるので吸着能力が向上するので好ましい。通常、貴金属やCo, Mn等が好ましい。また、ペロブスカイト化合物もNO<sub>x</sub>の吸着能があり、さらに炭化水素あるいはアルコール類とNO<sub>x</sub>の反応に活性を示すことが多いので好ましい吸着剤の候補である。

【0015】本方法においては、低濃度NO<sub>x</sub>含有ガス中のNOをコロナ放電またはオゾンの添加により、少なくとも一部をNO<sub>2</sub>に酸化した後、生成した該NO<sub>x</sub>(NO+NO<sub>2</sub>)含有ガスを吸着剤に接触させる方法も

(4)

特開平8-257351

5

NO<sub>x</sub>の吸着除去効果が高まるので有効な方法である。吸着されたNO<sub>x</sub>はNOに限らず、NO<sub>2</sub>の形態でもなら差し支えない。

【0016】吸着剤を還元剤を含有するガスで再生する場合、NO<sub>x</sub>の脱離と、NO<sub>x</sub>と炭化水素またはアルコール類との反応を効率良く進行させるため、あらかじめ加熱した再生用ガスを流通させることにより吸着剤が200～500℃の温度に昇温されることが好ましい。もちろん、他の手段、例えば電気ヒータ等により直接吸着剤を加熱してもよい。また再生用ガスを、吸着剤を含む閉鎖系内で循環使用し、吸着剤に吸着したNO<sub>x</sub>を十分に還元浄化することも好ましい方法である。この場合、適宜還元剤を添加していくのも良い。

【0017】本発明の還元剤として用いる尿素は、固体のまま再生用ガス中に噴霧混合しても良いし、水溶液の形態で供給しても良い。また、予め尿素の分解装置を設けておき、尿素を加水分解して生成したガスを適宜供給しても良い。尿素の分解生成物のうち、アンモニア、イソシアン酸等のアミン類はNO<sub>x</sub>の還元剤として用い得る。前記分解装置には、例えば加熱系内に水蒸気存在下で尿素を供給する装置や、加熱した尿素分解用触媒上に水蒸気存在下で尿素を供給する装置を用いることができる。

【0018】本発明の還元剤に用いる炭化水素としては、メタン、エタン、プロパン、ブタン、エチレン、プロピレン等の単体、あるいはLPGのような混合物でも良い。もちろんより炭素数の多い高級炭化水素でも良く、もちろんガソリン、灯油等の混合物でも良い。またアルコール類としては、メチルアルコール、エチルアルコール、プロピルアルコール等が使用出来、特にその種類に限定されない。

【0019】これらの炭化水素あるいはアルコールは、気体の場合はそのまま再生ガス中に供給すればよい。また、液体や固体の場合はその性状によって、再生ガス中へそのまま噴霧したり、適当な溶媒に溶かした後に供給することができる。

【0020】本発明の低濃度NO<sub>x</sub>除去方法において、吸着剤の再生を炭化水素あるいはアルコール類を含有するガスを流通させることによって行う際には、ガス中の酸素濃度を低くすることでより一層再生効率が向上する場合がある。例えばPt, Rh, Pd, Ru等の貴金属を含有する吸着剤によりNO<sub>x</sub>を吸着除去し、再生時に炭化水素を含有する窒素ガスを流通させた場合には、貴金属表面に吸着した酸素によってNO<sub>x</sub>還元反応が阻害され、反応効率が低下する場合がある。しかし、ガス中の酸素濃度を低くすると酸素による阻害が低減されるため、より効率良くNO<sub>x</sub>を還元し、吸着剤を再生することができる。

【0021】例えば一般に貴金属を含有する吸着剤の場合、再生処理時の流通ガス中の酸素濃度が0.5%以下

6

の場合に最も効率良くNO<sub>x</sub>を炭化水素で還元することができる。また、流通ガス中の酸素濃度が0.5%以上の場合であっても、酸素濃度が低いほど効率良くNO<sub>x</sub>を還元することが可能である。

【0022】また、貴金属を含有する吸着剤以外でも流通ガス中の酸素濃度を低減することで効率良くNO<sub>x</sub>を還元することができる場合がある。

【0023】吸着剤再生時の流通ガス中の酸素濃度を低減する方法には多様な方法がある。例えば炭化水素などを燃焼して酸素濃度を低減する方法、PSA法等の吸着剤を用いる方法、あるいは窒素ガスや炭酸ガスなどの不活性ガスのタンクを設けておき、吸着剤再生時に炭化水素と混合して流通させる方法等がある。

【0024】本発明の方法で還元剤として用いる化合物は、吸着剤上でのNO<sub>x</sub>の還元分解を促進するだけでなく、NO<sub>x</sub>の脱離も促進する。そのため、前記化合物を吸着剤からのNO<sub>x</sub>脱離促進剤として用い、吸着剤の再生をより低温で行うことも可能となる。この場合、一部のNO<sub>x</sub>が還元されずに吸着剤から脱離する場合もあり、後流にNO<sub>x</sub>還元工程を設ける必要があるが、脱離促進剤を使用しない場合に比較して還元工程を簡略化することが可能である。

【0025】

【作用】本発明による方法ではNO<sub>x</sub>の吸着剤の再生時に還元剤を含有するガスで再生するため、再生が容易に進む。これらの成分を含有しない再生ガスを用いた場合とは異なり、50～200℃の比較的低い温度域でもNO<sub>x</sub>の放出が起こる。これは吸着剤に、NO<sub>x</sub>と還元剤との反応を促進する触媒作用を持つ成分を添加しているため、吸着されているNO<sub>x</sub>は単に脱離するのではなく、吸着剤上である一定温度以上になると還元剤である炭化水素またはアルコール類との反応によりN<sub>2</sub>に分解されるため、脱離しやすくなるものと考えられる。

【0026】本方法では脱離するNO<sub>x</sub>はその場でN<sub>2</sub>に還元分解され、殆ど排ガスには含有されない。従って、通常のNO<sub>x</sub>吸着剤の再生時には脱離する高濃度NO<sub>x</sub>の後処理装置が必要となるが、本発明による方法では不要となる。

【0027】

【実施例】

(実施例1) 本発明になるNO<sub>x</sub>除去システムの一例を図1の全体フローにより説明する。低濃度NO<sub>x</sub>を含有する排ガス1は、酸化工程2でオゾナイザ3により合成されたオゾンと混合され、一部またはすべてのNOがNO<sub>2</sub>に酸化される。酸化工程2を流出したガスは吸着層4に導入され、NO<sub>x</sub>が吸着除去された後、換気塔5より大気中に放出される。

【0028】前記吸着層4は複数のユニットより成り、NO<sub>x</sub>が多量に吸着して吸着能力の低下したユニットは抜き出して後述する再生処理を実施する。

(5)

特開平8-257351

7

8

【0029】窒素6をファン7で吸着剤再生工程に導入し、吸着層4より抜き出した吸着剤ユニット8を流通させる。ユニット8内部の酸素濃度が十分に低下した時点で炭化水素9を窒素気流中に導入し、加熱装置10で約200℃に加熱、流通させる。ユニット8上でNO<sub>x</sub>は炭化水素によりN<sub>2</sub>に還元分解される。分解後のガスは再び吸着層4の上流に導入される。分解後のガスに未反応のNO<sub>x</sub>及び炭化水素が残留していた場合は吸着層4で吸着処理された後換気塔5より大気放出される。再生処理の終了したユニット8は再び吸着層4に組み込む。

【0030】本システムにより低濃度のNO<sub>x</sub>を効率よく吸着除去し、また吸着剤に吸着したNO<sub>x</sub>も速やかに還元して無害化することが可能となる。

【0031】（実施例2）本発明になるNO<sub>x</sub>除去システムの一例を図2の全体フローにより説明する。低濃度NO<sub>x</sub>を含有する排ガス1は吸着層4に導入され、ここでNO<sub>x</sub>が吸着除去された後換気塔5より大気放出される。吸着層4は複数のユニットより成り、NO<sub>x</sub>が多量に吸着して吸着能力の低下したユニットは抜き出して後述する再生処理を実施する。

【0032】窒素6をファン7によりユニット8に導入し、さらに吸着層4の上流に導入する。ユニット8内部の酸素濃度が十分に低下した時点で流路切り替えバルブ11、12を、吸着剤ユニット8から流出したガスが循環して再び8に流入するように切り替える。加熱装置10で約200℃に加熱したガスをファン7で循環流通させ、8をNO<sub>x</sub>の還元分解に必要な温度まで加熱する。同時に炭化水素9を循環系内に導入し、8より脱離するNO<sub>x</sub>を、脱離と同時にN<sub>2</sub>に還元分解する。NO<sub>x</sub>が十分に還元浄化され、再生が完了した8は再度吸着層4に組み込む。

【0033】本方法により低濃度のNO<sub>x</sub>を効率よく吸着除去でき、またNO<sub>x</sub>吸着後の吸着剤に循環系による加熱再生処理を行うことで、NO<sub>x</sub>を吸着剤上で浄化することができる。

【0034】（実施例3）本発明で用いる窒素酸化物吸着剤を下記のように調製した。

【0035】酸化イットリウム23g、酸化バリウム3\*

$$\text{NO}_x\text{除去率} = \frac{(\text{入口ガス中のNO}_x) - (\text{出口ガス中のNO}_x)}{(\text{入口ガス中のNO}_x)} \times 100(\%)$$

…(数1)

【0041】ここでNO<sub>x</sub>はNOとNO<sub>2</sub>の合計濃度(ppm)を表す。

【0042】表2に各温度に設定した吸着剤1の、ガス流通15時間後におけるNO<sub>x</sub>吸着除去率を示す。吸着剤1は、室温付近の温度域で高いNO<sub>x</sub>吸着性能を有することが分かった。

【0043】

【表2】

50

\*1g、酸化銅16gを、ライカイ機で1時間混練した。混練生成物を150℃で2時間乾燥した後、500℃で2時間予備焼成した。得られた酸化物を乳鉢で十分に粉砕した後、さらに870℃で4時間焼成した。次に、得られた粉末を直径45mmの円盤状にプレスし、これを破砕して粒径0.5～1mmの粒状に整粒した。この化合物は、YBaCuO<sub>7-x</sub>の組成を有し、X線回折測定の結果、ペロブスカイト型の結晶構造を有する複合酸化物であることが分かった。

【0036】前記の粒状YBaCuO<sub>7-x</sub>に所定量のジニトロジアミン白金酸水溶液を含浸した。これを150℃で2時間乾燥した後500℃で2時間焼成して、吸着剤1を得た。化学分析の結果、白金(Pt)はYBaCuO<sub>7-x</sub>に対して0.1重量%担持されていた。

【0037】（実施例4）吸着剤1のNO<sub>x</sub>の吸着性能を測定した。吸着剤1の4mlを、内径20mm、長さ800mmの石英ガラス製円筒管の中央部に充填し、表1の条件でNO含有ガスの処理を行った。なお、吸着剤の温度は、熱電対を挿入して測定した。また、石英ガラス製円筒管の入口及び出口ガス中のNO<sub>x</sub>(NO及びNO<sub>2</sub>)濃度は、化学発光式窒素酸化物分析計で連続計測した。

【0038】

【表1】

表 1

試験ガス組成	
NO	5 ppm
O <sub>2</sub>	20 %
水蒸気	3 %
N <sub>2</sub>	残 部
空間速度	10000 h <sup>-1</sup>
吸着温度	25～100℃

【0039】NO<sub>x</sub>除去率は次式に従って算出した。

【0040】

【数1】

表 2

吸着温度	NO除去率
25	97 %
50	95 %
100	68 %

(6)

特開平8-257351

9

【0044】（実施例5）吸着剤1を用い、実施例4と同様に25℃で15時間NO<sub>x</sub>含有ガスを流通させて吸着処理を施した後、再生処理を以下の方法で行った。

【0045】NO<sub>x</sub>吸着処理後の吸着剤1を充填した石英ガラス製円筒管内に、表3に示す、プロピレンを含有する窒素ガスを充填し、循環ポンプを用いて円筒管の一端から流出したガスを他端に戻して循環させた。円筒管を200℃まで加熱して30分間再生処理をした。

【0046】再生処理後に円筒管内のガスを採取してNO<sub>x</sub>濃度を計測した結果、0.1ppm以下であった。また、再生処理後の吸着剤1を窒素気流中で700℃まで昇温したが、吸着剤からのNO<sub>x</sub>の脱離は認められなかった。これらの結果から、上記の再生処理により吸着剤1に吸着したNO<sub>x</sub>は、ほとんど脱離して窒素に分解したことが分かった。

【0047】

【表3】

表 3

試験ガス組成	
プロピレン	1000ppm
N <sub>2</sub>	残部
空間速度	2000h <sup>-1</sup>
再生温度	200℃

【0048】（実施例6）吸着剤1を用い、実施例4と同様に25℃で15時間NO<sub>x</sub>含有ガスを流通させて吸着処理を施した後、再生処理を以下の方法で行った。

【0049】前記吸着剤1を充填した石英ガラス製円筒管内に、表4に示すように還元剤を含有しない窒素を充填し、循環ポンプを用いて円筒管の一端から流出したガスを他端に戻して循環させた。同時に円筒管を200℃まで加熱して、30分間再生処理をした。

【0050】再生処理後に円筒管内のガスを採取してNO<sub>x</sub>濃度を計測した結果、約13ppmであった。この結果、再生処理ガス中に炭化水素酸素が含まれないと一部またはすべてのNO<sub>x</sub>は充分に還元されないまま吸着剤1から脱離することが分かった。

【0051】

【表4】

表 4

試験ガス組成	
N <sub>2</sub>	100%
空間速度	2000h <sup>-1</sup>
再生温度	200℃

10

【0052】（実施例7）本発明で用いるNO<sub>x</sub>吸着剤を下記のように調製した。

【0053】市販の粒状γ-Al<sub>2</sub>O<sub>3</sub>を乳鉢で破碎して粒径0.5～1mmの粒状に整粒した。これに所定量のジニトロジアミン白金酸水溶液を含浸し、150℃で2時間乾燥した。さらに500℃で2時間焼成して、吸着剤2を得た。化学分析の結果、白金（Pt）はAl<sub>2</sub>O<sub>3</sub>に対して0.1重量%担持されていた。

【0054】（実施例8）実施例7においてジニトロジアミン白金酸水溶液に代えて硝酸コバルト水溶液を用いたほかは実施例7と同様にして吸着剤3を得た。硝酸コバルト水溶液の量及び濃度は、吸着剤3に含有されるコバルトが10重量%となるように調整した。

【0055】（実施例9）市販の、Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>比が約30であるZSM-5ゼオライト粉末を所定量の硝酸銅水溶液と乳鉢で混練し、150℃で2時間乾燥した後500℃で2時間焼成して、吸着剤4を得た。硝酸銅水溶液の量及び濃度は、吸着剤4に含有される銅が10重量%となるように調整した。

20 【0056】（実施例10）吸着剤2～4について、25℃において実施例4と同様の条件でNOの吸着実験を15時間実施した結果を表5に示す。いずれの吸着剤も高い吸着能を有していることが分かった。

【0057】

【表5】

表 5

吸着剤	NO除去率
吸着剤2	94%
吸着剤3	92%
吸着剤4	98%

【0058】（実施例11）実施例10でNO<sub>x</sub>吸着処理を施した吸着剤2～4について、プロピレンに代えてエチレンを用いた他は実施例5と同様の条件で吸着剤の再生実験を行った。再生処理後に石英ガラス製円筒管内のガスを採取して、NO<sub>x</sub>濃度を測定した結果を表6に示す。いずれの吸着剤も、吸着したNO<sub>x</sub>が脱離する際に同時に分解して窒素に変換されていることが分かった。

【0059】

【表6】

(7)

特開平 8-257351

11  
表 6

吸着剤	再生処理後ガス中の NO濃度
吸着剤 2	0.2 ppm
吸着剤 3	0.2 ppm
吸着剤 4	0.1 ppm

【0060】（実施例 12）実施例 10 で NO<sub>x</sub> 吸着処理を施した吸着剤 2～4 について、プロピレンに代えてエチルアルコールを用い、窒素に代えて空気を用いた以外は実施例 5 と同様の条件で吸着剤の再生実験を行った。再生処理後に石英ガラス製円筒管内のガスを採取して、NO<sub>x</sub> 濃度を測定した結果を表 7 に示す。いずれの吸着剤も、吸着した NO<sub>x</sub> が脱離する際に同時に分解して窒素に変換されていることが分かった。

【0061】

【表 7】

表 7

吸着剤	再生処理後ガス中の NO濃度
吸着剤 2	0.3 ppm
吸着剤 3	0.4 ppm
吸着剤 4	0.2 ppm

【0062】（実施例 13）吸着剤 1 について、25℃において、NO に代えて NO<sub>2</sub> を使用した以外は実施例 4 と同様の条件で NO の吸着実験を所定の時間実施した結果を表 8 に示す。吸着剤 1 は高い NO<sub>2</sub> 吸着能を有していることが分かった。

【0063】

【表 8】

表 8

吸着時間 (hr)	NO 除去率
15	98%
48	95%
96	88%

【0064】（実施例 14）実施例 13 で、NO<sub>2</sub> 吸着処理を 25℃ で 15 時間施した吸着剤 1 について、実施例 5 と同一条件での再生実験を行った。再生処理後に石英ガラス製円筒管内のガスを採取して NO<sub>x</sub> 濃度を計測した結果、約 0.2 ppm であった。また、再生処理後の吸着剤 1 を窒素気流中で 700℃ まで昇温したが、NO<sub>x</sub> の吸着剤からの脱離は認められなかった。この結果よ

12

り、NO<sub>2</sub> が吸着した吸着剤も本発明の方法によって再生処理が可能であり、NO<sub>2</sub> を NO と同様に吸着剤上で還元浄化できることが分かった。

【0065】（実施例 15）実施例 10 において NO を吸着させた吸着剤 4 を用い、再生実験を行った。

【0066】吸着処理後の吸着剤 4 を充填した石英ガラス製円筒管内に、表 9 に示す組成のガスを充填し、循環ポンプを用いて円筒管の一端から流出したガスを他端に戻して循環させた。円筒管を 200℃ まで加熱して 30 分間再生処理をした。

【0067】還元剤として用いた尿素は水溶液として保管しておき、400℃ に加熱した尿素分解用石英ガラス管内に所定量を滴下して加水分解した後、他のガス成分と混合した。

【0068】再生処理後に円筒管内のガスを採取して NO<sub>x</sub> 濃度を計測した結果、0.1 ppm 以下であった。この結果より、還元剤に尿素を用いて、NO を吸着剤上で還元浄化できることが分かった。

【0069】

【表 9】

表 9

試験ガス組成	
尿 素	500 ppm
水 蒸 気	3 %
O <sub>2</sub>	20 %
N <sub>2</sub>	残 部
空間速度	2000 h <sup>-1</sup>
再生温度	200℃

【0070】

【発明の効果】本発明によれば、低濃度 NO<sub>x</sub> を浄化処理する際に吸着剤以外に触媒層を設ける必要がないため、コンパクトかつ効率的な浄化処理を行うことができ、特に自動車トンネルや地下駐車場などの排ガス脱硝に好適である。

【図面の簡単な説明】

【図 1】本発明になる低濃度 NO<sub>x</sub> 含有ガスの処理に用いる装置の概念図である。

【図 2】本発明になる低濃度 NO<sub>x</sub> 含有ガスの処理に用いる装置の概念図である。

【符号の説明】

1…低濃度 NO<sub>x</sub> を含有する排ガス、2…酸化工程、3…オゾナイザ、4…吸着層、5…換気塔、6…窒素、7…ファン、8…吸着層 4 より抜き出した吸着剤ユニット、9…炭化水素、10…加熱装置、11、12…流路切り替えバルブ。



(8)

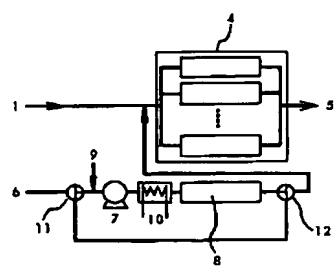
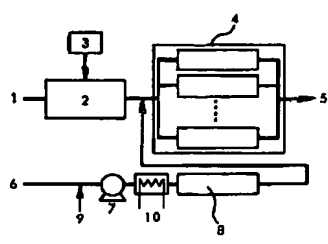
特開平 8 - 2 5 7 3 5 1

【図 1】

【図 2】

図 1

図 2



フロントページの続き

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